OA-25

Frozen superparaelectric state of the local polar domains in $GdMn_2O_5$ and $Gd_{0.8}Ce_{0.2}Mn_2O_5$

B.Kh. Khannanov, V.A. Sanina, E.I Golovenchits, M.P. Scheglov

Ioffe Institute, 194021, St. Petersburg, Russia
khannanov@mail.ioffe.ru

The results of a comparative study of the magnetic and dielectric properties, as well as the electric polarization of $GdMn_2O_5$ (GMO) and $Gd_{0.8}Ce_{0.2}Mn_2O_5$ (GCMO) multiferroics have been studied in the temperature range 5-330 K. These compounds belong to the class of multiferroics, in which the ferroelectric ordering with Curie temperatures T_C = 30-35 K is induced by a special type of magnetic ordering with close magnetic ordering temperatures [1]. GMO and GCMO have a central symmetry at room temperature (space group Pbam), which forbids the existence of electrical polarization. To explain the observed low-temperature ferroelectric ordering, an exchange striction model caused by the alternation of the nearest pairs of Mn^{3+} and Mn^{4+} ions with ferromagnetic strong double exchange and weak antiferromagnetic indirect exchange was proposed. The exchange striction along the b axis violates the lattice central symmetry, inducing ferroelectric ordering with polarization along the b axis [2]. The close temperatures of magnetic and ferroelectric ordering provide the appearance of a strong magnetoelectric coupling and the ability to control the state of GMO and GCMO both by magnetic and electric fields, which is attractive from an applied point of view. However, it is desirable to have such properties at higher temperatures. It has been found that the local polar domains exist in the multiferroics under study due to the phase separation process. The local phase separation domains occur due to the presence of the same number of Mn^{3+} and Mn^{4+} ions in GMO and in GCMO the number of Mn^{3+} ions prevail over Mn^{4+} ions due to the doping of GMO with Ce^{4+} ions. As a result, the same phase separation domains appear in GCMO, but their concentration is higher compared to GMO. The phase separation domains exist in the studied multiferroics in a wide temperature range from the lowest to room temperature. It was of interest to compare the results of electrical polarization studies in GMO and GCMO having different concentrations of polar domains of the same nature. The Mn^{3+} ions contain $3t_{2g}$ and $1e_g$ electrons on the 3d shell, while the Mn^{4+} ions have only $3t_{2g}$ electrons and an empty orbital doublet. The final probability of $1e_g$ electrons tunneling between Mn^{3+} and Mn^{4+} ions and deformations of the octahedra into which Mn^{3+} ions fall upon the recharging of Mn^{4+} ions by the $1e_g$ electrons lead to the energetic advantage of forming phase separation domains in which Mn^{3+} and Mn^{4+} ion pairs and their recharging electrons are accumulated. This process is similar to that which takes place in manganites with colossal magnetoresistance $LaAMnO_3$ (A = Sr, Ca, Ba) [3]. The phase separation domains in GMO and GCMO turned out to be polar and have ferromagnetic correlations, i.e. multiferroic ones. These domains form the superparaelectric state, which at temperatures $T \leq T_{fr} >> T_C$ represents the frozen superparaelectric state, in which electric polarization loops with residual polarization were observed. Such type state was previously considered theoretically [4], but was not observed experimentally. The temperatures T_{fr} correspond to the condition $kT_{fr} \approx E_A$, where E_A is the activation barrier at the boundaries of the phase separation domains [4, 5]. It turned out that the polarization and T_{fr} temperature values were differed for GMO and GCMO. Polarizations were greater, but temperatures of them existence were lower in GCMO. Electric polarization was measured by two different methods: the method of thermally stimulated pyro-current and the method of hysteresis loops (PUND – positive up negative down-method). It made it possible to separate the contributions to the polarization of the low-temperature polar order of the exchange-striction nature and the frozen superparaelectric state of the local polar domains. This also made it possible to understand the properties of polarizations of local polar domains, which arise at different ways of applying an external electric field in these two methods (when measuring static and dynamic polarization). The PUND method of measuring hysteresis loops allows one to subtract the parasitic contribution of the local conductivity of the phase separation regions. The influence of the magnetic field H on the polarization induced by the phase separation domains was found. The magnetic field increased the polarization and the temperature T_{fr}, to which hysteresis loops were observed. It was also found that a uniform, single-domain polar order occurs at $T < T_C$

in a strong internal field of the staggered field type without the application of an external electric field (at $E = 0$), which was first established by us when measuring the polarization by the pyro-current method without preliminary polarization of the sample in the E field $\neq 0$. The field E began to influence only near T_C, when the internal field sharply decreased and fluctuations appeared.

This work was supported by RFBR (Grant N 18-32-00241).

1. Y. Noda, H. Kimura, M. Fukunaga, et al., *J. Phys . Condens. Matter* **20**, 434206 (2008).
2. J. van den Brink and D.I. Khomskii, *J. Phys. Cond. Matter* **20**, 434217 (2008).
3. M.Yu. Kagan and K.I. Kugel', *Phys. Usp*. **44**, 553 (2001).
4. M.D. Glinchuk, E.A. Eliseev, A.N. Morozovska, *Phys. Rev. B* **78**, 134107 (2008).
5. V.A. Sanina, B.Kh. Khannanov, E.I. Golovenchits, et al., *Phys. Solid State* **60**, 537 (2018).